

Quasi-chemical approximation for nonrandomness in the hole theory of polymeric systems: application to homopolymer/random copolymer blends

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QUASI-CHEMICAL APPROXIMATION FOR NONRANDOMNESS IN THE
HOLE THEORY OF POLYMERIC SYSTEMS: APPLICATION TO HOMOPO-
LYMER/RANDOM COPOLYMER BLENDS

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ABSTRACT: The non-random-mixing version of the Holey-Huggins theory is used to extract molecular parameters from the experimental equation of state data of polystyrene, poly(p-bromostyrene) and a random copolymer poly(styrene-co-p-bromostyrene) of known composition. With these parameters upper critical miscibility behavior, in qualitative agreement with experimental observations, is predicted for the system poly(styrene-co-p-bromostyrene)/polystyrene. Quantitative agreement can be obtained for the equation of state and miscibility behavior if small changes in the values of the cross parameters are allowed.

INTRODUCTION

Miscibility in polymer blends, in which at least one component is a random copolymer, has drawn much attention in recent years (Ref.1), due to the so-called "repulsion effect" (Ref.2). According to this effect, miscibility can occur in these blends for a suitable choice of the copolymer composition without the presence of any specific interaction. This phenomenon was rationalised by different research groups (Refs.3-5) using lattice models based on the Flory-Huggins theory. Panayiotou extended the lattice fluid theory to random copolymer mixtures (Ref.6). This model is very successful and retains the simplicity of the lattice fluid theory. In this paper, a recently developed hole theory which accounts for non-random-mixing (Refs. 7-9) is used to describe and predict the equation of state behavior of homopolymers, random copolymers and the miscibility behavior of random copolymer/homopolymer blends.

THEORY: HELMHOLTZ FREE ENERGY OF RANDOM COPOLYMER/HOMO-
POLYMER BLENDS

Consider mixtures of a random copolymer A $P(A_1\text{-co-}A_2)$ with repeat units A_1 and A_2 and a homopolymer B. The mole fraction of A_1 segments in the copolymer is denoted by P_1 . The free energy of the random copolymer/homopolymer blends reads

$$\begin{aligned}
 A/n\langle s \rangle RT = & \phi_A \ln \phi_A + \phi_B \ln \phi_B + \frac{1}{\langle s \rangle} \ln y + \frac{1-y}{y} \ln(1-y) - \frac{(1-\langle \alpha \rangle y)}{\gamma y} \ln(1-\langle \alpha \rangle y) \\
 & - \frac{z(1-\langle \alpha \rangle)}{2q} [2u_1 \ln u_1 + 2u_2 \ln u_2 + 2v \ln v + 2w \ln w - (u_1 - \bar{X}_1 - \bar{X}_2 - \bar{X}_3) \ln(u_1 - \bar{X}_1 - \bar{X}_2 - \bar{X}_3) \\
 & - (u_2 - \bar{X}_1 - \bar{X}_4 - \bar{X}_5) \ln(u_2 - \bar{X}_1 - \bar{X}_4 - \bar{X}_5) - (v - \bar{X}_2 - \bar{X}_4 - \bar{X}_6) \ln(v - \bar{X}_2 - \bar{X}_4 - \bar{X}_6) \\
 & - (w - \bar{X}_3 - \bar{X}_5 - \bar{X}_6) \ln(w - \bar{X}_3 - \bar{X}_5 - \bar{X}_6) - 2 \sum \bar{X}_i \ln \bar{X}_i] - \langle c_s \rangle \ln \{ \langle v \rangle \bar{\omega} [1 - \beta (1 - \frac{\bar{X}}{q})]^3 \} \\
 & + \frac{\langle c_s \rangle}{2T} (1 - \frac{\bar{X}}{q}) (A \bar{\omega}^{-4} - 2B \bar{\omega}^{-2})
 \end{aligned} \tag{1}$$

where the \bar{X}_i are microscopic parameters used in the enumeration of contacts (see Tab.2). These parameters express the deviations from randomness and are obtained from quasi-chemical equations (Refs.7-9). The physical meaning of the other symbols is explained in Appendix.

The first five terms on the r.h.s. in Eq. (1) represent the combinatorial entropy of random-mixing of holes with homopolymer and copolymer segments. The terms in the square bracket account for the extra contribution due to non-random-mixing of holes and the different kind of segments. The remaining terms stem from the contribution of free volume and internal energy. Notice that in the above equations, the flexibility parameter $\langle c_s \rangle$ is defined by eq.(2)

$$\langle c_s \rangle = (c_{sA1} \phi_{A1} + c_{sA2} \phi_{A2} + (\delta_{cs} - 1)(c_{sA1} c_{sA2})^{1/2} \phi_{A1} \phi_{A2}) \phi_A + c_{sB} \phi_B \tag{2}$$

Here, c_{sA1} (c_{sA2}) is the flexibility parameter of the respective homopolymers $P(A_1)$ and $P(A_2)$; ϕ_{A1} (ϕ_{A2}) is the segment fraction of A_1 (A_2) in the pure copolymer. Eq.(2) expresses the assumption that a copolymer comprising segments A_1 and A_2 is characterised by a different flexibility parameter than a physical mixture of homopolymers $P(A_1)$ and $P(A_2)$. This is reflected in the copolymer parameter δ_{cs} (Ref.9).

Tab. 2 Enumeration of contacts in random copolymer/homopolymer blends

kind of contact pairs	number of contact pairs
segments a_1 - a_2 or segments a_2 - a_1	QX_1
segments a_1 -b or segments b- a_1	QX_2
segment a_1 -hole or hole-segment a_1	QX_3
segments a_2 -b or segments b- a_2	QX_4
segment a_2 -hole or hole-segment a_2	QX_5
segment b-hole or hole segment b	QX_6
segments a_1 - a_1	$Q(u_1 - \bar{X}_1 - \bar{X}_2 - \bar{X}_3)$
segments a_2 - a_2	$Q(u_2 - \bar{X}_1 - \bar{X}_4 - \bar{X}_5)$
segments b-b	$Q(v - \bar{X}_2 - \bar{X}_4 - \bar{X}_6)$
hole-hole	$Q(w - \bar{X}_3 - \bar{X}_5 - \bar{X}_6)$

UCMT MISCIBILITY BEHAVIOR OF THE BLEND POLY(STYRENE-CO-P-BROMOSTYRENE)/STYRENE

As an example of the application of the present theory, we have investigated miscibility behavior of the blend poly(styrene-co-p-bromostyrene)/polystyrene (P(S-co-pBrS)/PS). The molecular parameters for PS (ϵ_{A1A1}^* , v_{A1A1}^* and c_{sA1}) and P(pBrS) (ϵ_{A2A2}^* , v_{A2A2}^* and c_{sA2}) are estimated from the experimental PVT data and are shown in Tab.2. The cross parameters (ϵ_{A1A2}^* , v_{A1A2}^* and δ_{cs}) may be obtained from the experimental PVT data of a copolymer with given copolymer composition P(S(.84)-co-pBrS(.16)). The cross parameter values obtained in such a way are shown in Tab. 3. The agreement between experimental and theoretical PVT behavior is excellent and typical of hole theories (Ref.10).

Tab.2. Molecular parameters for PS and P(pBrS)

	ϵ_{ii}^* (10^4 J/mol)	v_{ii}^* (10^{-4} m ³ /mol)	c_s
PS	0.88463	0.95249	1.3198
P(pBrS)	1.22930	1.14970	1.8394

Tab.3. Cross parameters styrene/p-bromostyrene obtained from the experimental PVT data or miscibility behavior. ($\delta\epsilon = \epsilon_{a1a2}^* (\epsilon_{a1a1}^* \epsilon_{a2a2}^*)^{1/2}$ and $\delta_v = v_{ii}^* / ((v_{ii}^*)^{1/3} + v_{ii}^*) / 2)^3$)

	δ_c	δ_v	δ_{cs}
PVT	1.0251	1.0230	0.76839
Miscibility	1.0201	0.98721	0.76839

With all the parameters so far obtained, it is possible to predict miscibility behavior of the blend P(S-co-pBrS)/PS by the present theory. Fig.1 shows the predicted UCMT spinodal curve for the blend P(S(.71)-co-pBrS(.29)) /PS. The predicted critical temperature is obviously too high compared to the experimental maximum temperature ($T_{max} \approx 492$ K) which is assumed to be the consolute state for this system. However, the present theory does predict the occurrence of UCMT phase behavior for this system. The relative accuracy of the molecular parameters extracted from PVT data of the pure components (homopolymers and copolymers) is approximately 0.1%. If allowance is made for small changes in the cross interactional parameters (δ_v and δ_c), the experimental UCMT miscibility gap can be described quite accurately. The cross parameters obtained in this way are shown in Tab. 3 and the predicted equation of state behavior of the copolymer is shown in Fig.2. The predicted PVT behavior is practically indistinguishable from the PVT description with the parameters obtained from PVT behavior.

Note that we have kept the value of δ_{cs} unchanged during the calculation.

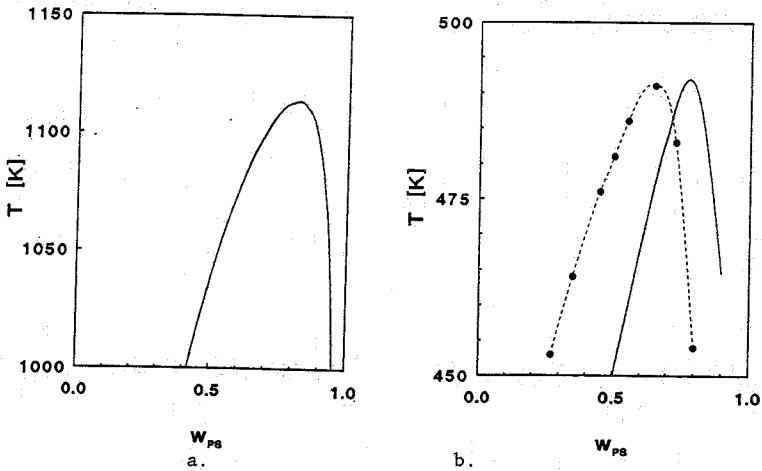


Fig.1. Miscibility behavior for the system PS/P(S(.71)-co-pBrS(.29)). (a) Predicted; (b) Adjusted; (---) experimental data (Ref.11); (____): computed.

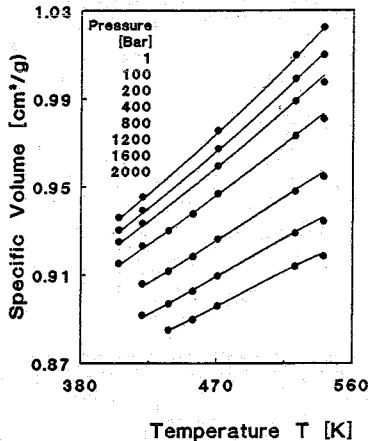


Fig. 2. Predicted equation of state behavior of the random copolymer P(S(0.84)-co-pBrS(0.16)). ●: experimental data (Ref12); (____): predicted.

CONCLUSIONS

With the molecular parameters extracted from the experimental PVT data of polystyrene(PS), poly(p-bromostyrene) (PpBrS) and poly(styrene-co-p-bromostyrene) (P(S-co-pBrS)), UCMT phase behavior is predicted, which is in agreement with experimental observations. A much more precise description of the UCMT phase behavior is realised, when the values of the cross

interactional parameters are obtained from the maximum temperature of the experimental cloud point curves. The PVT behavior of the random copolymer predicted with these cross parameters is in quantitative agreement with the experimental data.

Molecular parameters obtained from equation of state data are not sufficiently accurate to predict miscibility behavior quantitatively. However, the basic phase behavior is predicted. On the other hand, if miscibility data are used to extract cross parameters, the equation of state behavior of the copolymer is predicted quantitatively. With the present quasi-chemical hole theory a consistent description and prediction of PVT and miscibility behavior is obtained.

In principle, the theory can be readily extended to random copolymer/copolymer blends. This is left for further exploration.

APPENDIX: LIST OF SYMBOLS

ϕ_A (ϕ_B):	the segment fraction of component A (B)
$\langle s \rangle$:	the average number of segment per molecule
y :	occupied site fraction
$\langle \alpha \rangle$:	an auxiliary parameter, defined by $\langle \alpha \rangle = \gamma(1-1/\langle s \rangle)$
γ :	an auxiliary parameter, defined by $\gamma = 2/z$
z :	the coordination number of the lattice
u_1 :	contact site fraction of component A_1 in the copolymer
u_2 :	contact site fraction of component A_2 in the copolymer
v :	contact site fraction of homopolymer B
w :	contact site fraction of holes
$\langle c_s \rangle$:	the average flexibility parameter
$\langle v^* \rangle$:	the average hard core volume of each segment in the blend
$\bar{\omega}$:	reduced cell volume
β :	an auxiliary parameter, defined by $\beta = 2^{-1/6} \bar{\omega}^{-1/3}$
\bar{T} :	reduced temperature

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